Thickness mod ulated structural and photo-luminescence properties of magnetron sputtered nanocrystalline SiC ultrathin films

Narendra Singh and Davinder Kaur*

Functional Nanomaterials Research Lab, Department of Physics and Centre for Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India

*Corresponding author; Tel: (+91) 1332-2285407; Fax: (+91) 1332-273560; E-mail: dkaurfph@iitr.ac.in

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Abstract

Ultrathin silicon carbide (SiC) films were grown on p type Si (100) substrate by RF magnetron sputtering at constant substrate temperature of 700^0C for investigating thickness dependence of structural and photoluminescence properties. The structural and Photoluminescence properties were measured by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and photospectrometer respectively. X-ray diffraction pattern revealed (102) and dominant (105) reflections which corresponds to 4H-SiC and an enhancement in (105) peak intensity with increasing thickness was also observed. The thickness measured by X-ray reflectometry (XRR) reduces from ~ 46 nm to 12 nm by decreasing deposition time (40-10 minute) which in turn reduces the crystallite size. Photoluminescence spectra show a broad peak extending from ultraviolet to blue region centered at ~ 385 nm for film of thickness ~ 46 nm (deposition time 40 min). A shifting in Photoluminescence peak towards shorter wavelength (blue shift) with decreasing SiC ultrathin film thickness was observed, which could be attributed to quantum confinement effect. The improved Photoluminescence in ultrathin nanocrystalline SiC films could make it a potential candidate in optoelectronic and biomedical applications. Copyright © 2017 VBRI Press.

Keywords: Thin films, sputtering, XRD, XRR, photoluminescence.

Introduction

Silicon carbide (SiC), one of the wide band gap semiconductor have a large variety of applications in high power and high frequency electronics at elevated temperatures, photonic devices and light emitting diodes (LED) due to their superior thermal, mechanical, electronic and optical properties **[1-3].** Recently SiC has attracted special attention toward quantum repeaters, photonic quantum information processing, and biomedical applications such as drug delivery and bioimaging **[4-5]**. The indirect band gap of bulk SiC leads to weak optical transitions responsible for photoluminescence (PL), which are applicable in optoelectronic devices **[6]**. However, the SiC based nanostructures such as nanowires, nanotubes and nanobelts exhibit improved PL due to quantum confinement and large surface to volume ratio **[7]**. Fabrication of these nanostructures is somewhat complex, and requires highly expansive techniques along with high process temperature which make it unsuitable for large scale production. The fabrication of nanocrystalline SiC (nc-SiC) thin films by magnetron sputtering is relatively easier than these nanostructures (naowires, nanotubes and nanobelts). In our previous work we have deposited nc-SiC thin films which shows improved electrical properties **[8]**. Ultra-thin films (thickness<50nm) of nc-SiC may show quantum confinement effect, which could result in improved photoluminescence properties.

To date the photoluminescence properties of nc-SiC ultra-thin film were not studied. The main concern of this report is to reduce the thickness (from 46nm to 12nm) of SiC thin film in order to make it ultra-thin for investigating influence of confinement and size effect on structural and photoluminescence properties useful in optoelectronic, photonics and bioimaging applications.

Experimental

SiC ultra thin films were grown on P type Si (100) substrate by RF magnetron sputtering (Excel Instruments, India) using a commercial target of 4N purity SiC (ACI Alloys Inc. USA). The target used for fabrication of SiC ultrathin film was 5 cm in diameter and thickness of 3mm. Initially the Si substrates were thoroughly cleaned by ultrasonic bath with a mixture of distilled water and trichloroethylene in 4:1 ratio followed by washing in boiled acetone. The SiC target was kept at a distance of 4.5 cm from Si substrate in an on axis sputter up geometry arrangement. Before every deposition the sputtering chamber was evacuated to a base pressure of $2x10^{-6}$Torr. The chamber pressure was measured using a combination of pirani and penning vacuum gauges (Pfeiffer vacuum) and maintained at a constant pressure of 20 mTorr. The deposition was carried out at a RF power of 130W in pure argon atmosphere. During the deposition the substrate was kept at a constant temperature of 700^0C. The duration of SiC film deposition was varied from 10 minutes to 40 minutes to investigate thickness effect (<50nm) on properties of SiC thin film. All the deposition parameters are given in **Table 1.** The fabrication of SiC thin films is given elsewhere **[9]**.

Table 1. Deposition conditions for SiC thin films prepared by RF magnetron sputtering.

Substrate	P type Si (100)
Substrate temperature	973K
Target	SiC (99.99 % Pure)
Target-substrate (T-S) distance	4.5 cm
Base pressure	$2x10^{-6}$ Torr
Working pressure	20m Torr
Sputtering gas	Ar
Sputtering power	130W (RF)
Deposition time	10-40 minute

The orientation and crystallinity of SiC thin films were analysed by glancing incidence X-ray diffraction (GIXRD) (Bruker D-8 advanced) at grazing angle of 2^0 using CuKα (1.54Å) radiation at a step size of 0.02^0 with a count time of 2.5 seconds at each step. The SiC thin film phase confirmation was performed by Fourier transform infrared spectroscopy (FTIR) of Varian 608 IR spectrometer.

The FTIR spectra were recorded from 500 to 2500 cm^{-1} resolution averaging 100 scans. The thickness of SiC thin film was estimated by X-ray reflectrometry (XRR) (Bruker D-8 advanced). The Photoluminescence (PL) spectra were recorded by a FL-4600 Photospectrometer.

Results and discussion

The room temperature X-ray diffraction (XRD) pattern of SiC thin films grown on p-Si (100) substrate with varying deposition time from 10 to 40 minutes were shown in **Fig.1**. The XRD pattern shows (102) and dominant (105) reflections at 2θ ~38.3^0 and 57.2^0 which corresponds to hexagonal (4H-SiC) phase. The SiC thin film deposited for duration of 10 min. shows a weak intensity peak (105) only at 57.2^0. The film grown for deposition time more 10 min. revealed appearance of (102) reflection along with (105) reflection. The SiC thin film crystallinity increased evident from enhanced (105) peak intensity as the deposition time extends from 10 min. to 40 min. respectively. The average crystallite size was evaluated by XRD using Scherer's formula given as **[10]:**

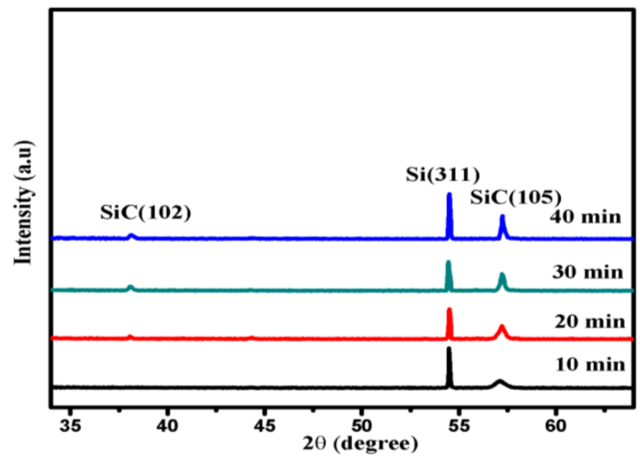


Fig. 1. XRD pattern of SiC thin films deposited at varying time (10-40min.); **Inset Fig. 1.** FTIR spectra of SiC film deposited for 40min.

$$t = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where λ is x-ray radiation wavelength (1.54 for $CuK_\propto$), β is full width at half maximum intensity (FWHM).

The average crystallite size calculated by Scherer's formula ranges from ~9 nm to 27 nm as the deposition time increases from 10 to 40 min. respectively shown in **Fig. 2(b)** and given in **Table 2**. The increased intensity and crystallite size of (105) reflection with deposition time may be explained as the time increased islands get enough time to grow which favors growth of larger crystallites and in terms increases the crystallite size.

Table 2. Values of SiC thin film thickness and crystallite size vs. deposition time.

Deposition time Min.	Thickness nm	Crystallite size nm
10	12	9
20	21	17
30	31	23
40	46	27

Inset of **Fig. 1** shows the FTIR transmission spectra of SiC ultra-thin film deposited for 40 min (thickness 46nm). The FTIR spectra revealed absorption bands at 600, 790 and 1025 cm^{-1} respectively, which corresponds to Si-Si stretching vibration, Si-C transverse optical phonon mode and Si-O stretching vibration mode respectively [**11-12**]. The Si-Si absorption band is attributed to p type Si (100) substrate. Si-O stretching band originated from native oxide layer in Si substrate. The presence of Si-C band is another evident of formation of pure SiC ultra-thin film in addition to XRD analysis.

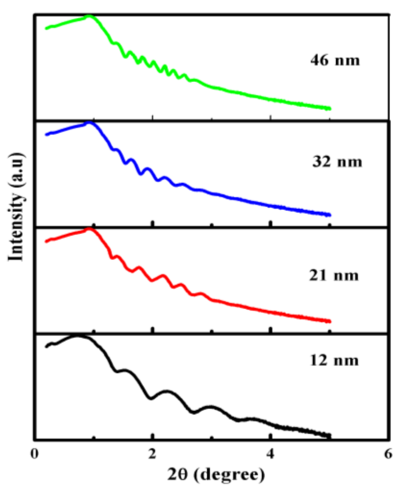
The thickness of SiC thin films was determined by X-ray reflectance (XRR) curves as shown in **Fig. 2(a)**. XRR is a nondestructive and non-contact technique used to measure thickness of thin films and multilayer's in range 2-200 nm with a precision of about 0.1-0.3 nm.

This technique also provides significant information about film and multilayer density and roughness with high precision. The XRR curves which consist of many Kiessig fringes are consequences of interference between X-rays reflected from film surface and film substrate interface. The surface and interface roughness play an important role in amplitude of Kiessig fringes. The Kiessig fringes observed when the X-ray incident angle is greater than a critical angle, the angle at which X-ray penetrates inside the material i.e. $\theta > \theta_c$. The widths and frequency of fringes depends on thickness of films, the width decreases and frequency increases as the film thickness enhanced. The thickness of SiC ultrathin films can be calculated as **[13]:**

$$d = \frac{\lambda}{(2\theta m{+}1 - 2\theta m)} \qquad (2)$$

Where d is thickness of film, λ is wavelength of X-ray (1.54A for CuK_{α}) and $2\theta\ m$ is m^{th} Kiessig fringe angular position. The thickness of SiC thin films estimated were ~ 12, 21, 32 and 46 nm for film deposited duration of 10, 20, 30, and 40 min. respectively. **Fig. 2(b)** shows the variation of SiC thin film thickness estimated from XRR measurement and crystallite size extracted from Scherer's formula with the deposition time. It is clear from **Fig. 2(b)** that the SiC film thickness and crystallite size reduces as the deposition time decreases.

(a)



(b)

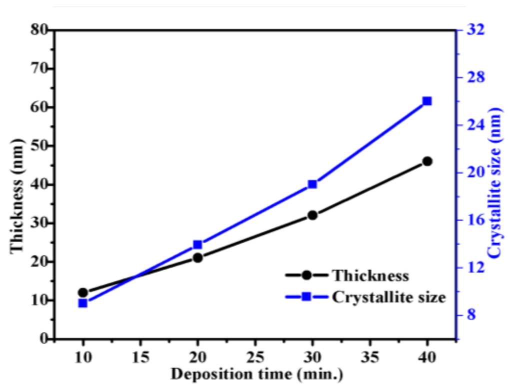


Fig. 2. (a) X-ray reflectance (XRR) plots of SiC thin films deposited for 10-40 minutes and **(b)** Variation of thickness and crystallite size as a function of deposition time.

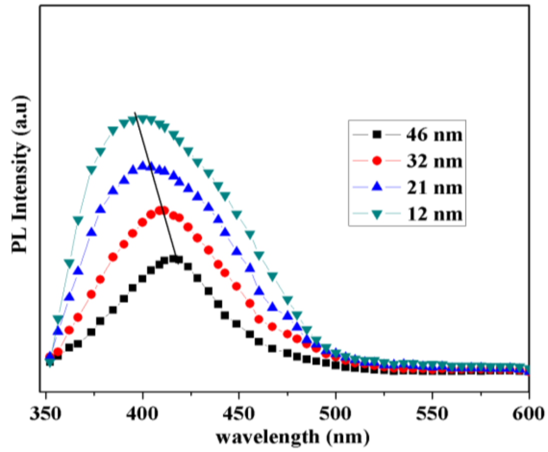


Fig. 3. Photoluminescence spectra of SiC ultra-thin films (~12-46 nm).

Fig. 3 depicts the room temperature PL spectra of nc -SiC ultra-thin films. SiC has a wider band gap (2.8-3.3 eV) in comparison to Si (1.1 eV), therefore PL peak of SiC can easily shift to lower wavelength (blue shift) as the crystallite size decreases to nano regime. It makes SiC suitable in UV or blue emitter in light emitting diode (LED) or display applications. SiC is also a good biocompatible material, used in biolabeling and biosensing application. The PL spectra shows a wide band centered at 385 nm (3.20 eV) close to band gap of 4H-SiC for the film deposited duration of 40 min (~46 nm). The observed PL in SiC thin films may be attributed to phonon assisted band to band recombination or a free to bound transition [**14**]. As the deposition time (thickness of film) reduced to 10 min (thickness ~12 nm), the peak shifts to a shorter wavelength with the increment in PL intensity. The increment in PL intensity and shifting toward shorter wavelength (blue shift) may be attributed to quantum confinement due to reduced crystallite size with decreasing SiC film thickness. This shifting in PL peaks indicates that it strongly depends on film thickness in nano regime where quantum size effect becomes significant.

Conclusion

In summary, sputtered deposited SiC ultra-thin films with varying thickness in the range ~12 to 46 nm were fabricated for study of its structural and optical properties. The XRD pattern revealed formation of 4H-SiC phase which was also confirmed by FTIR measurement. The XRR measurement exhibit SiC thin film deposited for a time span of 40 min were ~ 46 nm in thickness and decreases monotonically to a value of ~ 12 nm as the deposition time reduced to 10 min. A reduction in crystallite size with decrement in SiC thin film thickness was also observed. The decrement in crystallite size with reduction in SiC ultra-thin film thickness in nano regime was responsible for the observed shifting in photoluminescence spectra.

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